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Research Article

Synthesis and characterization of manganese tetroxide (Mn_3O_4) nanofibers by electrospinning technique

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Abstract: Manganese tetroxide (Mn_3O_4) nanofibers were prepared by electrospinning homogeneous viscous solution of 20 wt%, 28 wt% and 36 wt% manganese acetate in poly vinyl alcohol (PVA) and calcining the nanofibers at 1000 ℃ for 2 h. Electrospinning was carried out at 9 kV DC with tip to collector distance (TCD) of 7 cm. Thermo gravimetric analysis (TGA) of the fibers indicates the pure phase of manganese oxide above 500 ℃. XRD analysis of calcined (at 1000 ℃) nanofibers indicates the formation of phase-pure tetragonal Mn_3O_4. Scanning electron microscopy (SEM) studies show the fibers cylindrical with the diameters in the range of 100–600 nm and aspect ratio > 1000. In general, the average diameter of the green fibers decreases with the increase in manganese acetate concentration. The diameter of calcined nanofibers is reduced by 34%.

Keywords: electrospinning; manganese tetroxide; poly vinyl alcohol; nanofiber

1 Introduction

Manganese oxide is environmental friendly and abundantly available in nature. Due to good electromechanical performance, it is a promising electrode material for super capacitors and batteries [1,2]. It is also widely used as catalyst and for water filtration application [3]. There is a demand to develop advanced composite electrode materials using manganese oxide and carbon black as conductive additive to increase electronic conductivity of the composite electrode for improving power–energy characteristics of super capacitors. The efficiency of manganese oxide increases in nanofiber form due to its large surface area. Among various options, electro-spinning is the simplest and extensively used technique to produce nanofibers in the last 10–15 years [4–7]. This technique is used for preparation of polymer nanofibers [8] as well as preparation of metal oxide/ceramic nanofibers (e.g., alumina, zirconia, titania, nickel oxide, lead zirconate titanate, barium titanate, tin oxide, samarium oxide) [9–18]. Lei *et al*. [19] tried to grow ultrathin MnO_2 nanofibers on the graphitic hollow carbon spheres (GHCS) by stoichiometric redox reaction between GHCS and MnO_2. The porous GHCS serves as an excellent conductive substrate for rapid electron transfer and the ultrathin MnO_2 nanofibers grown on GHCS provide large electrochemically active surface area for fast reaction. Razak *et al*. [20] reported that they used manganese dioxides together with polyaniline and CNTs to form nanocomposites which improved the electron conductivity. Shao *et al*. [21] reported

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preparation of Mn_2O_3 and Mn_3O_4 nanofibers from manganese acetate and explained that the phase and morphology were largely influenced by the calcination temperature. However, there is hardly any study about the effect of processing parameters such as concentration of salt solution on the morphology of manganese oxide nanofibers. Therefore, in this study, an attempt has been made to study the effect of concentration of salt solution or solid loading on morphology of green and heat-treated manganese oxide nanofibers.

2 Experiment

2.1 Materials

Manganese acetate $Mn(CH_3COO)_2{\cdot}4H_2O$ (99.0% purity, analytical reagent grade, Merck) and poly vinyl alcohol (PVA) (*MW*=125 000, purchased from M/s. Loba Chemie) were used as starting materials without any further purification.

2.2 Preparation of the composite precursor solution

0.7 g of $Mn(CH_3COO)_2{\cdot}4H_2O$ was dissolved in 2 ml of distilled water. 12% PVA solution was prepared in distilled water. 10 ml of 12% PVA solution was mixed with already prepared manganese acetate solution and continuously stirred for 4 h to obtain viscous sol suitable for electrospinning. Similarly, two more sols of manganese acetate + PVA solution were prepared by taking 0.5 g and 0.3 g of $Mn(CH_3COO)_2{\cdot}4H_2O$ respectively. A flow sheet of solution preparation methodology is given in Fig. 1.

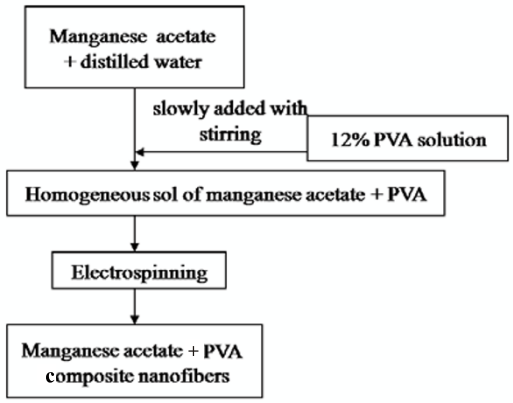

Fig. 1 Flow sheet for preparation of manganese acetate + PVA composite nanofibers.

2.3 Electrospinning of manganese acetate + PVA solution

About 3 ml of manganese acetate + PVA solution was taken in a syringe with fine capillary metallic needle. The electrospinning was carried out by maintaining tip to collector distance (TCD) of 7 cm and at a DC voltage of 9 kV. The flow rate of the solution was maintained at 0.5 ml/h. A schematic drawing of the electrospinning set up is presented in Fig. 2. The positive terminal of a high voltage source was applied to the needle of the syringe while the negative terminal was connected to the aluminium foil collector. The composite nanofibers of manganese acetate + PVA were prepared by subjecting the solution to a high electrical potential (9 kV) for 2 h. The details of the solution preparation methodology and electrospinning conditions are summarized in Table 1.

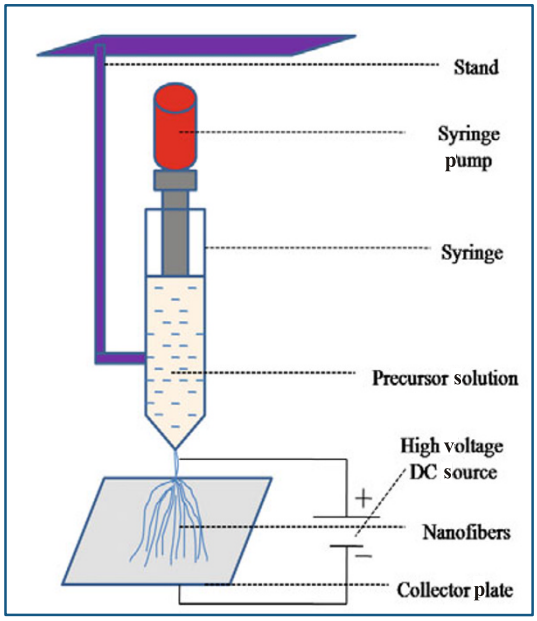

Fig. 2 Schematic drawing of the electrospinning set up.

Table 1 Solution preparation and electrospinning conditions

Chemical precursors	Preparation of solution	Electrospinning conditions
(1) Manganese acetate (2) Distilled water (3) Poly vinyl alcohol (*MW*~ 125 000)	(1) 20 wt%, 28 wt% and 36 wt% manganese acetate solution mixed with 10 ml of 12% PVA solution and stirred continuously for homogenization	(1) Nozzle diameter (internal)~0.5 mm (2) Tip to collector distance (TCD) ~7 cm (3) Voltage ~ 9 kV (4) Humidity ~ 50%–60% (5) Solution flow rate ~ 0.5 ml/h

3 Characterization

The manganese acetate + PVA composite nanofibers were subjected to thermo gravimetric analysis (TGA) using Universal V2.6D, TA Instrument. The sample holder was heated in air at a rate of 10 ℃/min, in the temperature range 50–800 ℃. The resulting TG curve is shown in Fig. 3. The composite nanofibers were calcined at 1000 ℃ for 1 h to study the sintering behavior of fibers. Phase analysis of the calcined nanofibers was carried out by X-ray diffractometer with Cu Kα ($\lambda = 1.5406$ Å) radiation in the range from 10° to 70° and at a scanning rate of 1 (°)/min. The resulting XRD pattern is presented in Fig. 4. The morphology of the fibers was ascertained using a scanning electron microscope (LEO 440i). The average fiber diameter and the distribution of fibers were determined using about 30 randomly selected fibers taken from SEM micrograph. The morphology of green nanofibers and their diameter distributions with change in PVA concentration are shown in Fig. 5. SEM photograph of sintered manganese oxide nanofibers

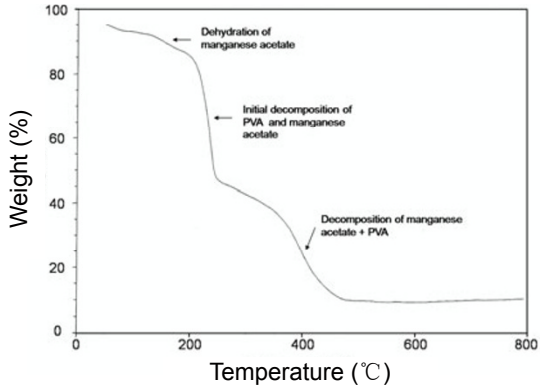

Fig. 3 Thermo gravimetric analysis of manganese acetate + PVA nanofibers.

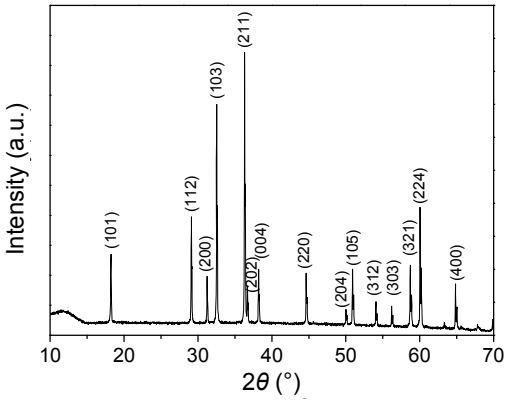

Fig. 4 X-ray diffraction pattern of manganese tetraoxide obtained after calcinations of manganese acetate + PVA nanofibers at 1000 ℃.

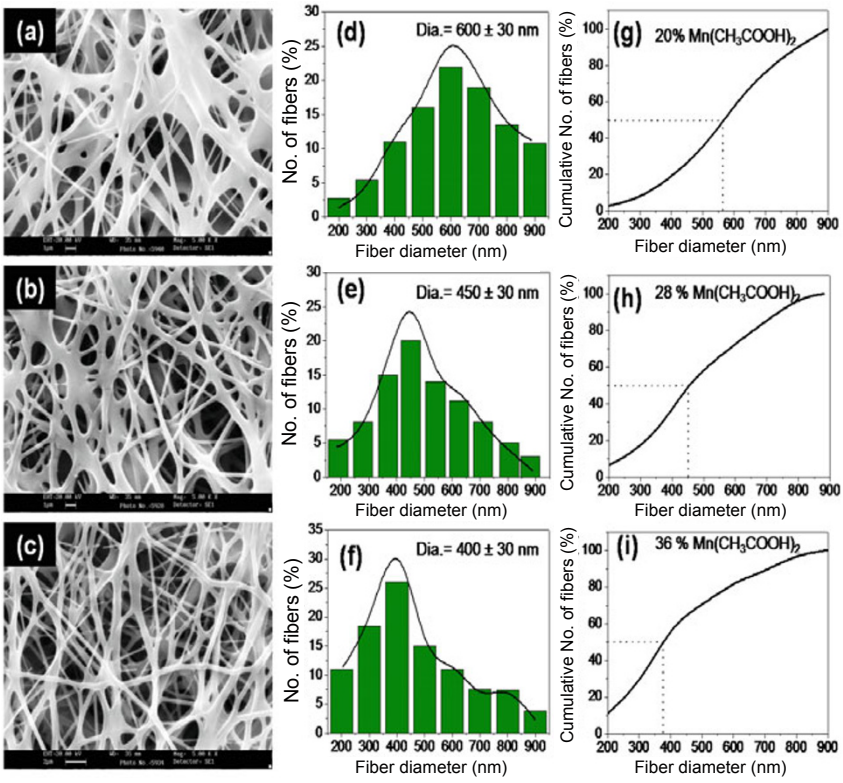

Fig. 5 SEM micrographs of manganese acetate + PVA nanofibers: manganese acetate concentration (a) 20 wt%, (b) 28 wt%, (c) 36 wt%; (d), (e), (f) their corresponding diameter distributions; (g), (h), (i) corresponding median diameters.

and its diameter distribution is presented in Fig. 6.

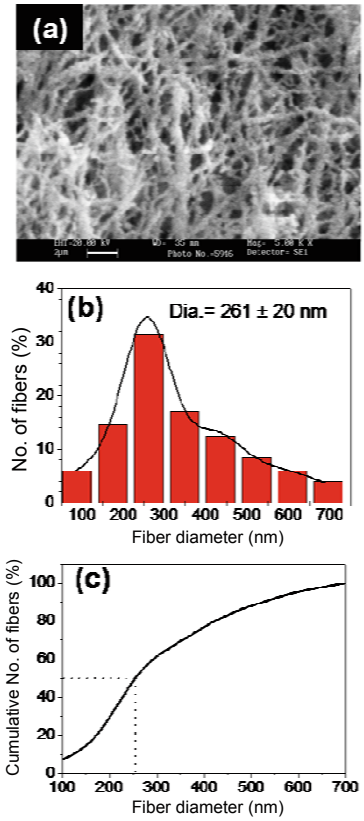

Fig. 6 SEM micrograph of manganese tetroxide nanofibers with diameter distributions after heat treatment at 1000 ℃ for 1 h.

4 Results and discussion

4.1 Thermo gravimetric analysis of manganese acetate + PVA nanofibers

From Fig. 3 it is observed that decomposition of manganese acetate + PVA proceeds in three steps. In the first step, dehydration of manganese acetate occured in the temperature range 100–190 ℃. In the second step, decomposition of PVA and manganese acetate started after 230 ℃ and the process of decomposition continued up to 480 ℃. The complete decomposition of PVA and manganese acetate occured below 500 ℃. Therefore, the calcination temperature was selected at much higher temperature (1000 ℃) to make sure that all the organics were expelled and also fibers were partially sintered for their easy handling.

4.2 XRD analysis

X-ray diffraction pattern of manganese acetate + PVA nanofibers calcined at 1000 ℃ was analyzed and the peak positions correspond to the tetragonal phase of Mn_3O_4. This observation was similar to that reported by Shao *et al.* [21].

4.3 Morphology study of manganese acetate + PVA composite nanofibers

From SEM photographs (Fig. 5) it is observed that the average fiber diameter decreases with the increase in manganese acetate concentration. This is mostly due to the increase in electrical conductivity of the solution with increasing salt concentration [22]. SEM photograph of the calcined nanofiber at 1000 ℃ (Fig. 6) shows the fibers retain their shape but with a rough surface due to the loss of organics leaving only Mn_3O_4 grains. The diameter of the sintered fibers is about 261 nm which is nearly 34% less compared to its green counterpart.

5 Conclusions

Manganese acetate + PVA composite nanofibers were successfully prepared by electrospinning technique and phase-pure Mn_3O_4 nanofibers were obtained after calcination at 1000 ℃. The average diameter of the fibers decreases with the increase of manganese acetate concentration. 34% shrinkage in the diameter was noticed after calcinations due to the loss of organics and partial sintering.

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